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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

: Docket 00740-451795

TALLON, Jeffery L.

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Application No. 10/010,746

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Filed: December 7, 2001

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For: NOVEL ORGANIC/INORGANIC OXIDE
MULTILAYER MATERIALS

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Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

CLAIM FOR PRIORITY

The Applicant in the above-identified application claims the benefit of priority under 35 U.S.C. §119 of New Zealand Application No. 508699 as set forth in the Declaration filed concurrently herewith. Pursuant to §119 and 37 C.F.R. §1.55, we are submitting a certified copy of the New Zealand priority application.

Respectfully submitted,

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Enclosure: Priority document.



CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 7 December 2000 with an application for Letters Patent number 508699 made by INDUSTRIAL RESEARCH LIMITED.

Dated 15 January 2002.

A handwritten signature in black ink, appearing to read 'Neville Harris'.

Neville Harris
Commissioner of Patents



508699

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Patents Form No. 4

PATENTS ACT 1953

25 **PROVISIONAL SPECIFICATION**

NOVEL ORGANIC/INORGANIC-OXIDE MULTILAYER MATERIALS

We, **INDUSTRIAL RESEARCH LIMITED**, a New Zealand company, of Gracefield
30 Road, Lower Hutt, New Zealand

do hereby declare this invention to be described in the following statement:

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INTELLECTUAL PROPERTY COUNCIL
- 7 DEC 2000
RECEIVED

FIELD OF INVENTION

The present invention describes novel self-assembling organic/inorganic-oxide multilayer materials based on single or multiple atomic layers of tungsten oxide, molybdenum oxide 5 or other metal oxides interspersed between organic spacer layers. These provide "plastic-like" materials with highly tuneable electronic properties suitable for electronic applications and especially *flexible* displays, electrochromic devices, sensors and logic and storage devices. In addition the two-dimensional character of these hybrid multilayers offers the possibility of a broad range of other applications including thermoelectric 10 coolers and possibly novel superconductors. The invention also encompasses other similar organic/ inorganic multilayer materials based on copper, nickel, manganese or ruthenium oxides which display exotic quasi-two-dimensional magnetic properties and superconductivity. The simplicity of their self-assembly, using solution-based fabrication, provides for a cost-advantage technology with all the benefits of plastics, especially 15 flexibility and ease of manufacture.

BACKGROUND

The development of organic conductors and semiconductors in recent decades has opened 20 the door to the possibility of flexible plastic displays and low-cost logic and storage devices [see for example P.Yam, 'Plastics get wired.' *Scientific American*, **273** (1), 74-79 (July 1995), or J.C. Scott, 'Conducting polymers: From novel science to new technology.' *Science*, **278** (5346), 2071-2072 (12 Dec 1997).]. There is much international effort to push these materials through to practical devices [see for example the above noted 25 references or: J. S. Miller, 'Conducting Polymers – materials of commerce', *Advanced Materials*, **5** (7/8 & 9), 587-589 & 671-676, (1993).]. The overwhelming significance of these developments has been recognised by the award of the Nobel Prize in Chemistry for the year 2000 to MacDiarmid, Heeger and Shirakawa, the discoverers of the conducting polymer polyacetylene [see for example R. F. Service 'Getting a Charge Out of Plastics' 30 *Science*, **290**, 425-427, (20 October 2000)]. However, a significant limitation in the use of organic semiconductors is their low electron mobility arising from the weak van der Waals bonding between neighbouring polymer molecules. This, in turn, limits device switching speeds. High electron mobility can be found in doped crystalline inorganic

oxides (because of their strong covalent bonding of their extended framework) but these materials demand high temperatures for synthesis and are brittle, non-flexible materials.

A specific example of such an oxide material is tungsten trioxide, WO_3 . This material
5 adopts a wide range of electronic properties ranging from an n-type semiconductor to a metal depending upon doping level. These doping states are accompanied by the well-known changes in colour observed in the so-called tungsten bronzes that have been used, for example, in pigments for paint. More advanced applications include architectural glazings, ophthalmic devices, instrumentation devices and displays. Tungsten trioxide has
10 a perovskite ABO_3 structure with the A-sites vacant, consistent with the 6+ valence state of W^{6+} . Each W ion is 6-fold coordinated to oxygen atoms in a roughly octahedral coordination. The octahedra are corner shared as shown by the schematic section in Figure 1 where the octahedra are represented by the corner shared diamonds. Electron doping into the conduction band is achieved by inserting additional cations into the otherwise
15 vacant 12-coordinated A sites. Molybdenum trioxide, MoO_3 , exhibits much the same chemistry and structure.

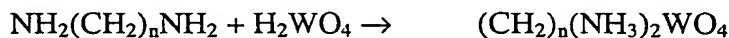
SUMMARY OF INVENTION

20 The present invention, by way of example, is directed to the fabrication of materials comprising two-dimensional single atomic layers of corner-shared WO_6 octahedra interspersed between organic spacer layers. Such a material offers the high electron mobility associated with the extended WO_6 sheets together with the flexibility associated with the organic spacer layers which facilitate the self-assembly of the hybrid materials.
25 Such atomically layered materials further provide enhanced and exotic electronic properties associated with the low dimensionality of the WO_6 sheets.

When a single atomic layer of WO_6 octahedra is formed then its chemical formula is WO_4^{2-} (the four in-plane oxygens all being shared by adjacent octahedra while the two
30 apical oxygens are confined wholly to a single octahedron). Thus two additional cation charges need to be supplied per formula unit to stabilise the structure. In the present invention these additional charges (providing the charge balance) are introduced using

ammonium ions positioned in the vacant A-sites above and below the WO_4^{2-} layer. These ammonium ions may terminate each end of an organic molecule as illustrated schematically in Figure 2 with the structure repeated indefinitely in the c-direction providing an organic/inorganic multilayered hybrid material where the organic spacer layer
 5 is a diammonium organic cation. Such a structure possesses highly anisotropic properties and strong two-dimensional in-plane electronic properties. The organic spacer molecules may be, for instance, a diammoniumalkane cation generally represented as $\text{NH}_3(\text{CH}_2)_n\text{NH}_3^{2+}$ and the hybrid compound may be synthesized for example by reacting a diaminoalkane with tungstic acid in solution, viz:

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We may read Mo (molybdenum) for W (tungsten) in all of the above considerations or these may be used in combination. Furthermore other high valency metals such as Ti, Nb,
 15 Ta, Ru, V and Re may be used in partial combination with Mo, W or both. Other known diammonium organic ions will also provide possible stabilising organic spacer molecules. For synthesis in solution tungstic or (molybdic) acid may be dissolved in ammonia solution or, alternatively, the metals W or Mo may be reacted with hydrogen peroxide to form peroxy polytungstate or peroxy polymolybdate acids as precursors. Other standard solution
 20 precursors for the metal oxide species will be known in the art.

Further novel compounds of the invention include higher-order organic/inorganic-oxide materials. These comprise multilayers of two or more adjacent sheets of WO_6 or MoO_6 octahedra separated by the organic spacer layer. Such materials are of general formula
 25 $\text{NH}_3\text{ANH}_3 \cdot \text{W}_m\text{O}_{3m+1}$ where $m=1, 2, 3, \dots, 6, \dots$ or, more specifically in the case of a diammoniumalkane spacer molecule, $\text{NH}_3(\text{CH}_2)_n\text{NH}_3 \cdot \text{W}_m\text{O}_{3m+1}$ where $m=1, 2, 3, \dots, 6, \dots$ A two-layer compound of this sort is shown schematically in Figure 3.

The novel material structures shown in Figures 2 and 3 may be described as *eclipsed*
 30 structures. The invention also comprises a class of *staggered* organic/inorganic-oxide hybrid materials where the organic spacer molecules are monoammonium organic molecules, A.NH_3^+ , which contain a single ammonium group. These may stack in

interdigitated configuration, with weak bonding between the organic molecules, to provide staggered oxide layers as shown in Figure 4.

The organic ammonium ions in these staggered structures may comprise an alkyl 5 ammonium ion, $\text{CH}_3(\text{CH}_2)_m\text{NH}_3^+$ with $m=1, 2, 3, \dots 12$, or an aromatic ammonium ion such as benzyl ammonium ion $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+$ or phenethyl ammonium ion $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$. Again higher-order structures, of general formula $(\text{A.NH}_3)_2\text{W}_n\text{O}_{3n+1}$, are included in the invention in which two or more oxide layers may be interspersed 10 between the organic spacer layers. A schematic example of the $n=2$, double layer compound is shown in Figure 5. The organic/inorganic-oxide hybrid compounds may be synthesized from solution using tungstic acid (or molydbic acid) and benzyl amine or phenethylamine.

It can be seen that these novel organic/inorganic-oxide compounds provide *great structural* 15 *diversity* which allows considerable control of the coupling between the oxide layers and hence the degree of anisotropy and the effective dimensionality of the electronic states. Moreover, as noted they may be constructed using W, Mo or any combination thereof and in addition other metallic cations such as Ti, Nb, Ta, Re, V and Ru, or other suitable metal, 20 may be incorporated to stabilise the structures and enhance their chemical stability, as well as dope the oxide layers to provide semiconducting or metallic properties. Electronic doping may also be achieved through incorporation of organic dopants such as methyl ammonium ions.

Further novel cuprate, nickelate, ruthenate and manganese-based organic/inorganic hybrids 25 are also included in the invention. The basic structure of the materials described above is contingent upon the octahedral oxygen coordination of a hexavalent cation such as W^{6+} or Mo^{6+} . Organic/inorganic-oxide structures may be fabricated with divalent cations such as Cu^{2+} and Ni^{2+} where these are coordinated into a corner-shared square-planar structure (i.e. with no apical oxygen) or with tetravalent cations such as Mn^{4+} or Ru^{4+} where these are 30 coordinated into a corner-shared square-pyramid structure. In both cases higher order structures with two or more oxide layers each separated by an alkali earth ion, preferably calcium, situated in the perovskite A-site, may be fabricated. The general formulae for

these additional novel materials are $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{CuO}_2$, $(\text{A}\cdot\text{NH}_3)_2\text{CuO}_2$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m}$, $m=1, 2, 3, \dots$, $(\text{A}\cdot\text{NH}_3)_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m}$, $m=1, 2, 3, \dots$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{NiO}_2$, $(\text{A}\cdot\text{NH}_3)_2\text{NiO}_2$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{Ca}_{m-1}\text{Ni}_m\text{O}_{2m}$, $m=1, 2, 3, \dots$, $(\text{A}\cdot\text{NH}_3)_2\text{Ca}_{m-1}\text{Ni}_m\text{O}_{2m}$, $m=1, 2, 3, \dots$, and $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{MnO}_3$, $(\text{A}\cdot\text{NH}_3)_2\text{MnO}_3$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{CaMn}_2\text{O}_6$, $m=1, 2, 3, \dots$, $(\text{A}\cdot\text{NH}_3)_2\text{CaMn}_2\text{O}_6$, $m=1, 2, 3, \dots$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{RuO}_3$, $(\text{A}\cdot\text{NH}_3)_2\text{RuO}_3$, $\text{NH}_3\cdot\text{A}\cdot\text{NH}_3\text{CaRu}_2\text{O}_6$, $m=1, 2, 3, \dots$, $(\text{A}\cdot\text{NH}_3)_2\text{CaRu}_2\text{O}_6$, $m=1, 2, 3, \dots$. The wide variety of these materials provide for different types of magnetic ordering (e.g. just by altering the structure from staggered to eclipsed) and other correlated states such as charge density waves and low-dimensional superconductivity. The discovery of surface superconductivity at 91K on the surface of lightly doped Na_xWO_3 single crystals [see Y. Levi et al., "Europ. Phys. Lett." **51**, 564 (2000)] raises the prospect of high temperature superconductivity in the present novel two-dimensional compounds.

The compounds of the invention may be incorporated into devices by the production of films using methods known in the art such as spin coating, dip coating, spraying, painting, printing and such like.

Their great utility is that they self assemble by precipitation out of solution. They may then be dissolved in organic solvents and spin-coated onto suitable substrates and for example onto single-crystal perovskite substrates, such as SrTiO_3 , with matching lattice parameters. The substrate lattice parameter may be selected to stabilise the films. Through careful heat treatment c-axis oriented films may be fabricated. Devices such as sensors, electrochromic films and thin-film field-effect transistors may be fabricated using these methods. Field-effect transistors may be made using the organic/inorganic-oxide as the semiconducting channel and device characteristics may be optimised by control of doping and of the spacing of the oxide layers. Sensor applications may be implemented based on the change in doping state induced by adsorbed gases.

BRIEF DESCRIPTION OF THE FIGURES

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In the figures:

Figure 1 shows a schematic diagram of the structure of WO_3 (or MO_3) in which the corner-shared WO_6 octahedra are represented by the light blue corner-shared diamonds. Doping is achieved by substituting cations into the vacant 12-coordinated perovskite A-sites.

5 Figure 2 shows a schematic diagram of the structure of the hybrid organic/ inorganic multilayered compound $\text{NH}_3\text{ANH}_3\cdot\text{WO}_4$ where $\text{NH}_3\text{ANH}_3^{2+}$ may be a diammoniumalkane chain. The single atomic layer of WO_6 octahedra are again represented by the light blue corner-shared diamonds and the NH_3^+ groups are represented by the red circles at either end of the alkane chains. The organic group A is represented by the blue ellipse.

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Figure 3 shows a schematic diagram of the structure of the two-layer hybrid organic/inorganic multilayered compound $\text{NH}_3\text{ANH}_3\cdot\text{W}_2\text{O}_7$ where $\text{NH}_3\text{ANH}_3^{2+}$ may be a diammoniumalkane chain. Symbols are as shown in Figure 2. In general, any number of oxide layers may be interspersed between the organic spacer layers providing the general formula $\text{NH}_3\text{ANH}_3\cdot\text{W}_m\text{O}_{3m+1}$.

15 Figure 4 shows a schematic diagram of the structure of the staggered hybrid organic/inorganic-oxide multilayered compound $(\text{ANH}_3)_2\text{WO}_4$ where A is an organic molecule represented by the blue ellipse. The WO_6 octahedra are again represented by the light blue corner-shared diamonds and the NH_3^+ groups by the red circles.

20 Figure 5 shows a schematic diagram of the structure of the 2nd member of the general staggered structural series $(\text{A.NH}_3)_2\text{W}_n\text{O}_{3n+1}$. The double layer of W_2O_7 is shown by the double layer of light-blue corner-shared diamonds and the interdigitated blue ellipses represent alkyl or aromatic organic groups terminated by ammonium ions (red circles).

Example

A quantity 3.429 g of H_2WO_4 was weighed out and dissolved in 60 ml of ammonia solution with gentle heating to 70°C. After cooling 3 ml of Benzylamine was added and the mixture stirred and heated under flowing nitrogen. The excess ammonia was evaporated off slowly, leaving the wet precipitate, which was then filtered and dried.

X-ray Diffraction was performed on the resultant white powder. The powder diffraction pattern revealed a major peaks corresponding to d-spacings of 16.48 Å and 15.59 Å. One of these, possibly the smaller, is consistent with the expected lattice parameter for dibenzylammonium tungstate, $(C_6H_5CH_2NH_3)_2WO_4$. The other compound is as yet
5 unidentified.

A film was made by redissolving some of the powder in anhydrous ethanol, spinning onto a $SrTiO_3$ single-crystal substrate at 2000 rpm and drying for 15 minutes under flowing nitrogen gas at 80°C.

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Ed Wood
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By the authorised agents
AJ PARK
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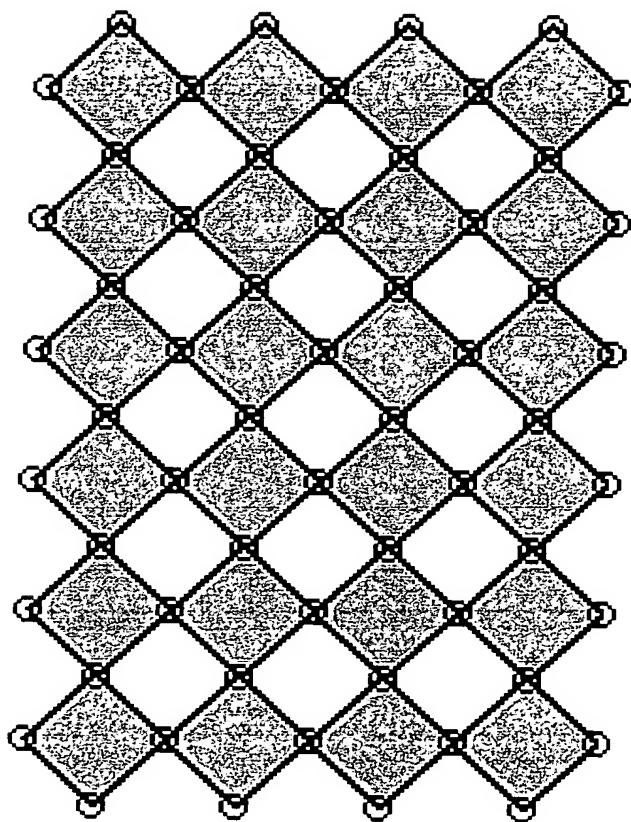


Figure 1

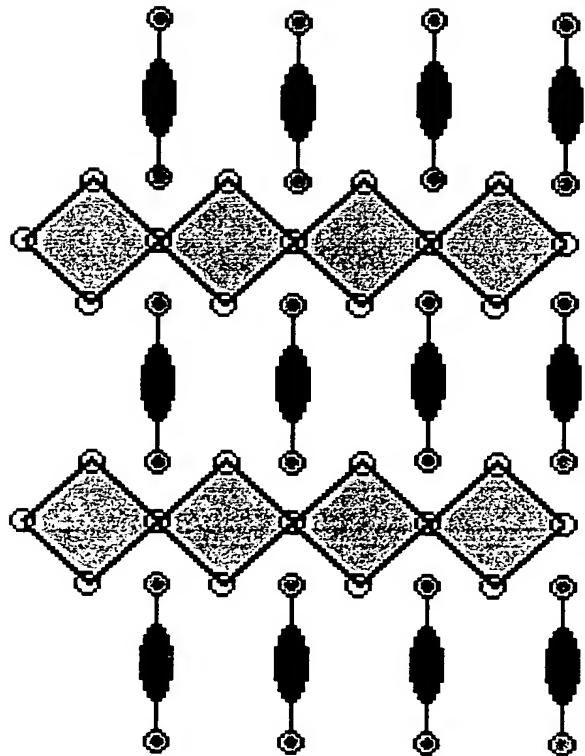


Figure 2

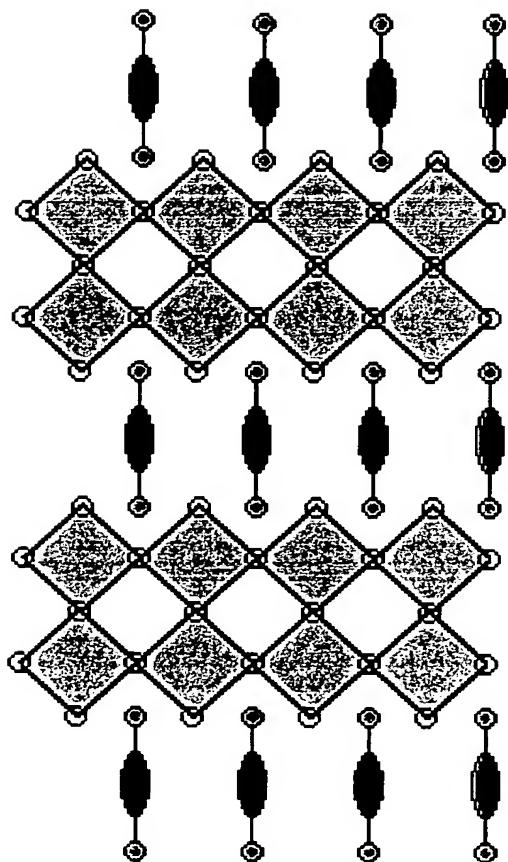


Figure 3

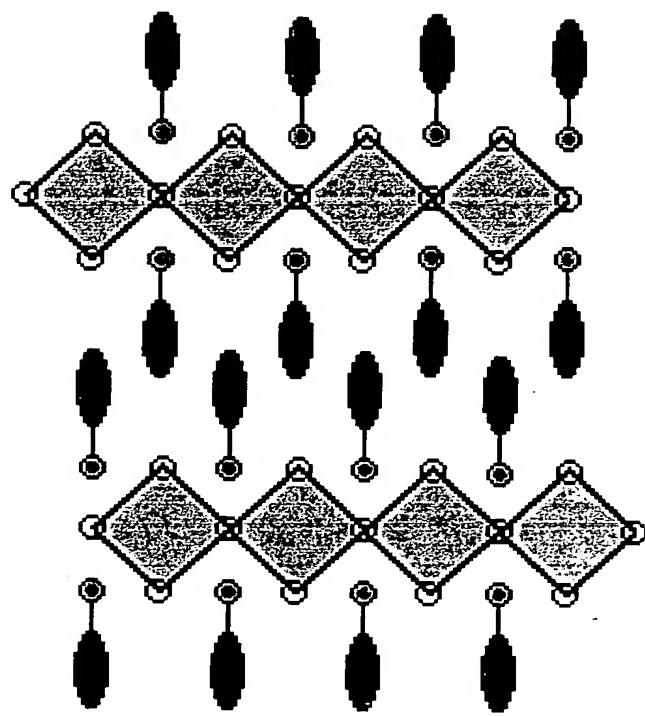


Figure 4

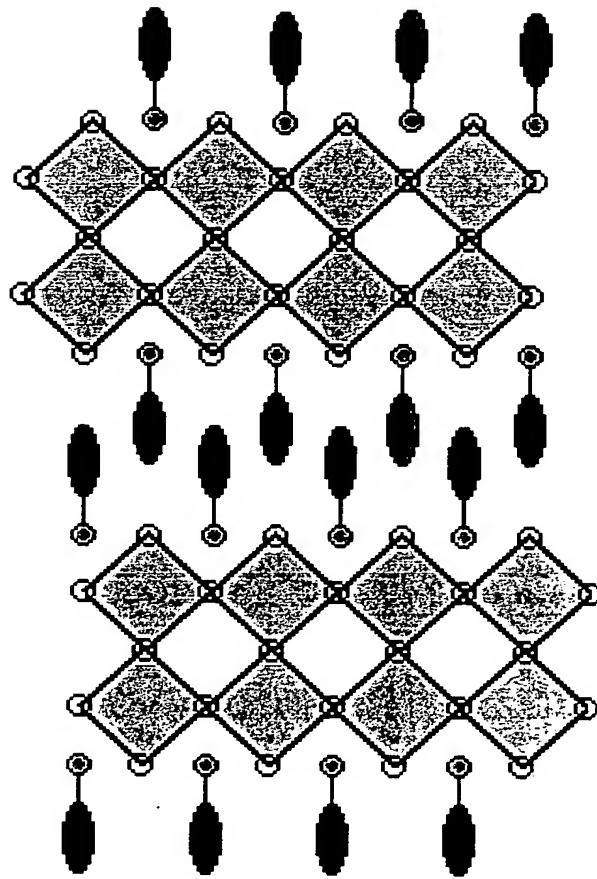


Figure 5